

# Development of nitrogen-doped carbons using the hydrothermal method as electrode materials for vanadium redox flow batteries

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**Abstract** Nitrogen-doped carbons are suggested as electrochemically active materials for V(IV)/V(V) redox couples for a vanadium redox flow battery (VRB). These materials were synthesized using a hydrothermal reaction of aqueous glucose solution in the presence of ethylenediamine as a nitrogen source. The physical and electrochemical properties of the nitrogen-doped carbons are characterized by cyclic voltammetry, high-resolution transmission electron microscopy and X-ray photoelectron spectrometry. These results reveal that the hydrothermal method is an effective way to synthesize high-content nitrogen-doped carbons. Nitrogen doping significantly improves catalytic activity and reversibility. Therefore, use of nitrogen-doped carbon is expected to increase the energy storage efficiency of VRBs.

**Keywords** Vanadium redox flow battery · Nitrogen-doped carbon · Nitrogen functional group · Pyridinic nitrogen · Hydrothermal reaction · Ethylenediamine

## 1 Introduction

The vanadium redox flow battery (VRB), utilizing the redox reaction of vanadium ions, has received a great deal of attention as a large-scale electrochemical energy storage system for load leveling and peak shaving [1, 2]. The VRB is a type of flow battery in which the reactant vanadium ions are stored in external tanks and supplied to the cell

containing the electrodes. The vanadium ions are dissolved in a highly acidic solution to increase the ionic conductivity of the electrolyte and to provide hydrogen ions to the reaction at the positive electrode. Use of a highly acidic electrolyte allows few materials to be employed as an electrode in the VRB. Typical electrode materials are therefore graphite-based materials such as graphite felt and powder [3, 4]. However, the poor electrochemical activity of carbon electrodes remains one of the technical barriers limiting the efficiency of VRB system.

In an attempt to improve the electrocatalytic activity of carbon electrodes, a great deal of research has been dedicated to functionalize the carbon surface through electrochemical or chemical treatment methods [5–7]. It is known that the electrochemical activity of carbon electrodes depends on the oxygen functional groups such as hydroxyl and carboxyl groups present on the surface [8–12]. These active groups are believed to electrochemically catalyze the redox reaction of vanadium ions.

Apart from oxygen functional groups, nitrogen-doped carbon materials have been reported to enhance the electrochemical activity of many electrochemical reactions including the oxygen reduction reaction [13–15]. This result inspired researchers to use nitrogen-doped carbons in the preparation of VRB electrodes [16]. Recently, mesoporous carbon was doped with nitrogen using  $\text{NH}_3$  by heat treatment and was tested in VRBs [17]. It was found that nitrogen doping is beneficial in increasing the electron transfer on electrode/electrolyte interfaces for the redox reaction of vanadium ions. However, this process requires high-temperature treatment at 850 °C, and the nitrogen content of 3.3 % is relatively low. Therefore, it is necessary to develop an easy and mild process for the synthesis of nitrogen-doped carbons with high concentrations of nitrogen functional groups.

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In this study, a nitrogen-doped carbonaceous material was prepared in an autoclave through a hydrothermal method in the presence of a chelating agent as the nitrogen source and was used as an electrode in a VRB. The nitrogen content was controlled by the amount of chelating agent, and the physical and electrochemical properties of the resulting materials were characterized by cyclic voltammetry (CV), high-resolution transmission electron microscopy (HR-TEM), and X-ray photoelectron spectrometry (XPS). The influence of the type and amount of nitrogen functional groups on the electrocatalytic activity of the redox reactions of V(IV)/V(V) was investigated in detail.

## 2 Experimental

The nitrogen-doped carbons denoted as N-carbon were prepared by a hydrothermal method in the presence of a chelating agent based on a previous report [18]. Glucose was dissolved in deionized water at a concentration of 1 M. Different amounts of ethylenediamine (ED) were added to the glucose solution to control the nitrogen content in the carbons. For the hydrothermal reaction, the prepared solution was placed in a Teflon-sealed autoclave, and the temperature was maintained at 180 °C for 6 h. The resulting precipitate after the hydrothermal reaction was centrifuged, washed with water and ethanol three times, and dried overnight at 80 °C. For comparison, pristine carbons were also prepared using the same procedure without the addition of ED.

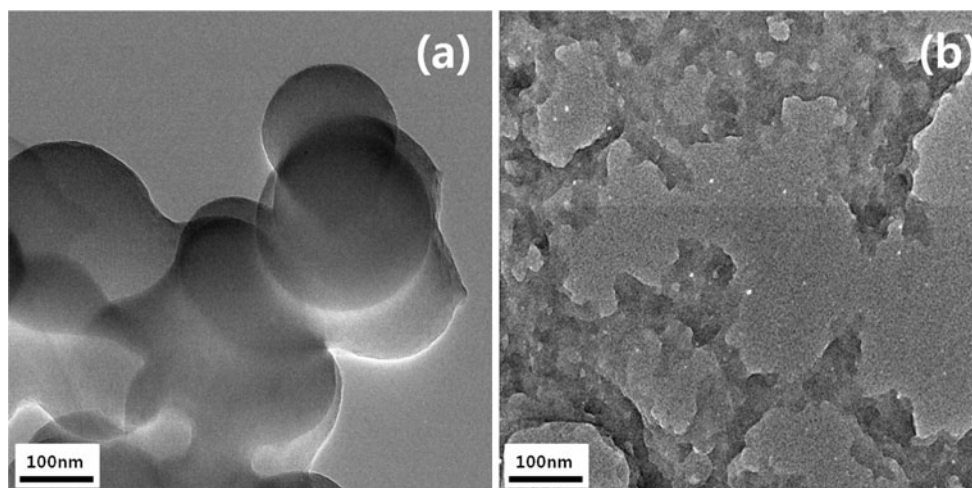
Cyclic voltammetry (CV) was used to determine the electrochemical activity of the V(IV)/V(V) redox reaction in 1 M VOSO<sub>4</sub> + 5 M H<sub>2</sub>SO<sub>4</sub> electrolyte using a conventional three-electrode system. Platinum wire and a standard Hg/HgSO<sub>4</sub> electrode served as a counter electrode

and a reference electrode, respectively. Potentials are reported with respect to a reversible hydrogen electrode unless otherwise noted. The working electrode was prepared by applying ink containing the prepared carbons to a glassy carbon disk in a rotating disk electrode, achieving 20 µg loading. The ink was prepared by ultrasonically dispersing 3.44 mg of the prepared carbons in a solution containing 0.5 mL of isopropyl alcohol (IPA), 1.5 mL of deionized water, and 50 mL of 5 wt% Nafion solution. The morphology of the prepared carbons was inspected with HR-TEM. XPS was performed to analyze the nitrogen-containing functional groups on the carbon surface.

## 3 Results and discussion

HR-TEM analysis was performed to characterize the morphology of carbons synthesized by the hydrothermal reaction in the presence and absence of ED. Figure 1 shows that the pristine carbons prepared without using ED have a spherical structure with a uniform size distribution of approximately 200 nm. In contrast, a dramatic structural change is observed when ED is added to the hydrothermal reaction. The introduction of ED converts the structure of the resulting carbon from a spherical shape to a net-cross structure with a continuous skeleton. It is believed that amine-containing molecules influence the conversion pathway of glucose to carbon during the hydrothermal reaction. BET measurements indicate that the specific surface area of N-carbon with 10 wt% ED is 1.7 m<sup>2</sup> g<sup>-1</sup>.

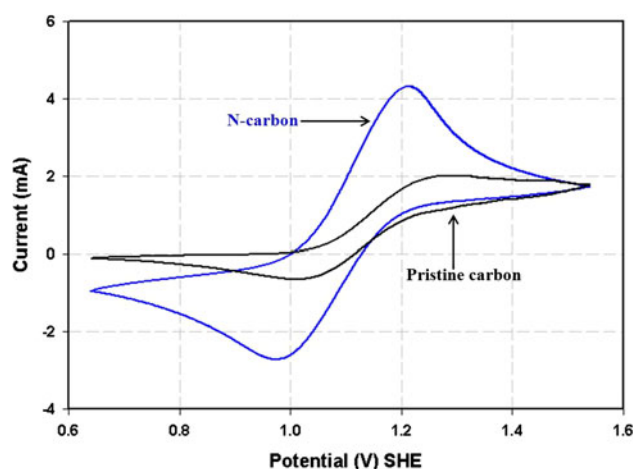
Figure 2 shows the CV of the N-carbon and pristine carbon in 1 M VOSO<sub>4</sub> + 5 M H<sub>2</sub>SO<sub>4</sub> electrolyte between 0.64 and 1.54 V versus SHE. The redox peaks are attributed to the V(IV)/V(V) redox reaction as follows:



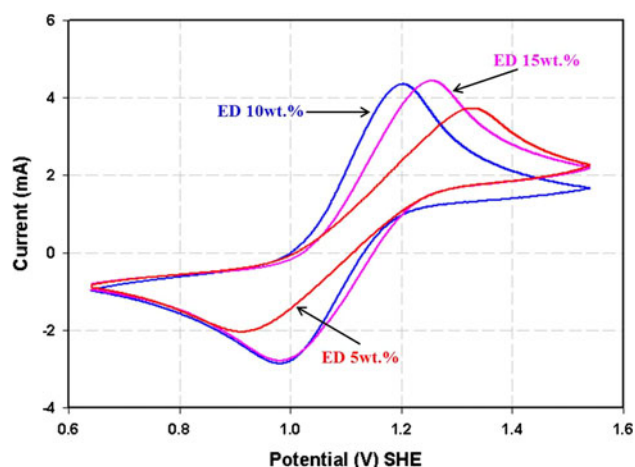
**Fig. 1** HR-TEM images of **a** pristine carbon and **b** N-carbon



It is obvious from Fig. 2 that the electrochemical activity of the redox reaction of vanadium is improved significantly after the pristine carbons are modified with ED. The oxidation and reduction peak currents of N-carbon with background subtraction are 4.15 and 3.74 mA, respectively, which are much higher than those of pristine carbon (1.91 mA for oxidation and 1.15 mA for reduction). In addition, the onset potential of the oxidation reaction shifts in the negative direction by 60 mV for the N-carbon, and the peak potential separation for the N-carbon (0.22 V) is smaller than that of the pristine carbon (0.27 V), implying that the redox reaction can occur more easily on the surface of N-carbon. The reversibility of the redox reaction can be estimated from  $I_{\text{pc}}/I_{\text{pa}}$ , the ratio of cathodic and anodic peak current. The ratio for N-carbon (0.9) is closer to 1 than that of pristine carbon (0.6), indicating that N-carbon is more reversible. Based on these results, it can be



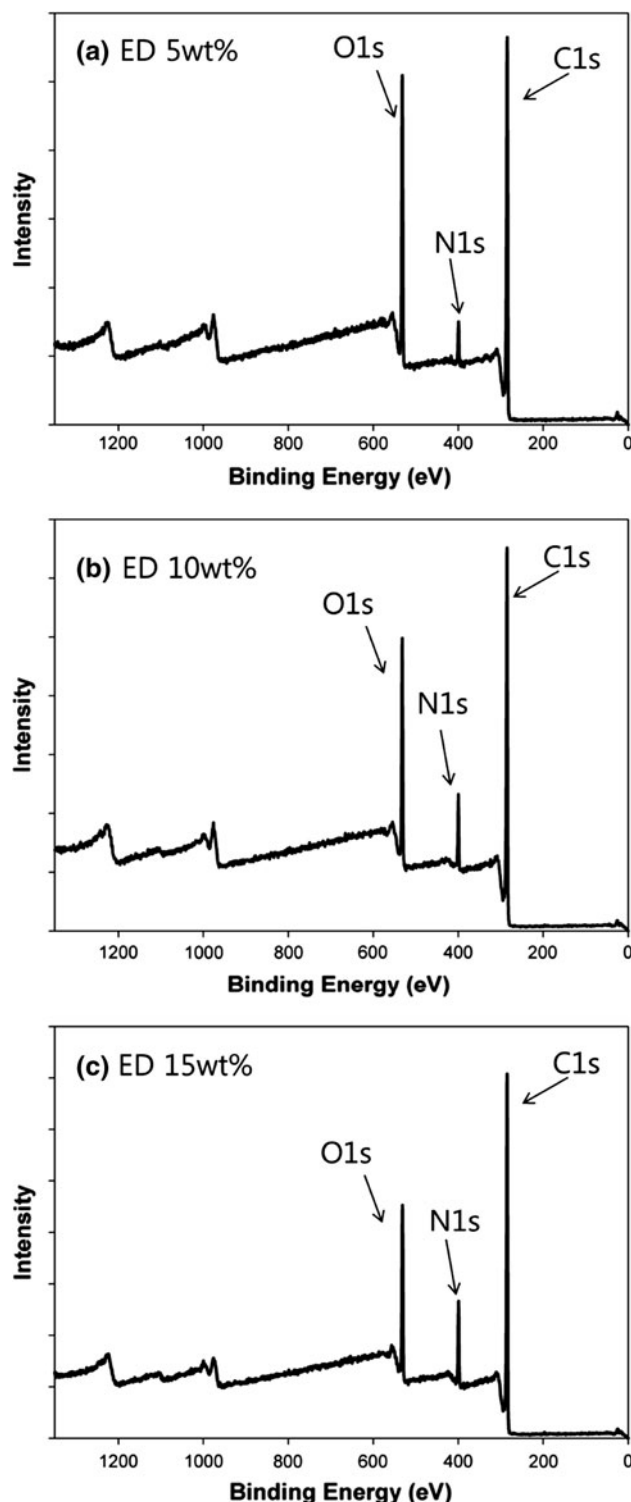
**Fig. 2** Cyclic voltammograms of pristine carbon and N-carbon at a scan rate of  $10 \text{ mV s}^{-1}$  in  $1 \text{ M VOSO}_4 + 5 \text{ M H}_2\text{SO}_4$



**Fig. 3** Cyclic voltammograms of N-carbons with different amounts of ED at a scan rate of  $10 \text{ mV s}^{-1}$  in  $1 \text{ M VOSO}_4 + 5 \text{ M H}_2\text{SO}_4$

concluded that N-carbon possesses higher electrocatalytic activity of the vanadium redox reaction and thus is beneficial for improving the energy storage efficiency of VRB.

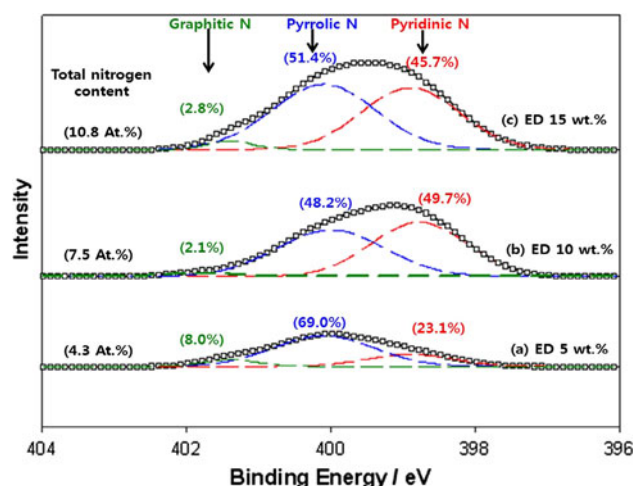
To further explore the effect of ED on the catalytic activity, N-carbons were prepared using different amount



**Fig. 4** Survey XPS spectra of N-carbon with different amount of ED

of ED from 5 to 15 wt% based on glucose, and their catalytic activities were evaluated with CV. As shown in Fig. 3, the redox current peaks increase, and the onset potential shifts to negative potential as the ED increases from 5 to 10 wt%, indicating that the catalytic activity is improved. In the case of 15 wt% ED, the peak anodic current is almost the same as that of 10 wt% ED. However, the onset potential moves in the positive direction.

It is well known that catalytic activity strongly depends on surface functionalities. To examine the surface composition change caused by the addition of ED, XPS was performed to analyze the nitrogen-containing functional groups. Figure 4 shows the survey XPS spectra of N-carbon with different amount of ED. The composition ratio for nitrogen, carbon, and oxygen is summarized in Table 1. No data are given for the pristine carbon because it does not exhibit the nitrogen peak. Since N-carbon was prepared at low temperature, high oxygen contents were observed from the N-carbons. As shown in Table 1, the nitrogen content present in N-carbon increases with the amount of ED. The nitrogen content in N-carbon is 7.5 % when 10 wt% of ED is used, which is a much higher value than 3.3 % for the  $\text{NH}_3$ -derived nitrogen-doped carbons, as reported in the literature [17]. This result reveals that nitrogen can be incorporated into the carbonaceous framework through a hydrothermal reaction using a chelating agent under mild conditions. To identify the type of nitrogen functional group, as shown in Fig. 5, the N 1s XPS spectra were deconvoluted into three peaks, which were assigned as pyridinic-N (398.3 eV), pyrrolic-N (400.1 eV), and graphitic-N (401.3 eV) [19]. It is seen that the portion of pyridinic-N is increased from 23.1 to 49.7 %, while the ratio of pyrrolic-N and graphitic-N is reduced as the amount of ED increases from 5 to 10 wt%. As the amount of ED increases to 15 wt%, however, the ratio of pyridinic-



**Fig. 5** XPS spectra of the N 1s region deconvoluted for N-carbons with **a** 5 wt% ED, **b** 10 wt% ED and **c** 15 wt% ED

**Table 1** Atomic ratio of the samples measured by XPS

	N (%)	C (%)	O (%)
N-carbon (ED 5 wt%)	4.71	69.15	26.14
N-carbon (ED 10 wt%)	7.52	74.4	18.08
N-carbon (ED 15 wt%)	10.87	74.09	15.04

N slightly decreases. Based on the catalytic activity evaluation with respect to the amount of ED as shown in Fig. 3, it is clear that pyridinic-N shows a strong correlation with the increase in catalytic activity. It has been reported that pyridinic-N promotes the activity of the oxygen reduction reaction due to its charge delocalization, which is beneficial to breaking the oxygen bonds [15, 20]. Similarly, it is believed that the pyridinic-N can behave as an active site for the redox reaction of vanadium ions by affecting the breaking and formation of V–O bonds. Considering low surface area of N-carbon, it is considered that the nitrogen functional groups are responsible for the enhanced catalytic activity.

## 4 Conclusion

Nitrogen-doped carbons were prepared by a hydrothermal reaction in the presence of glucose and the chelating agent ED, which serves as a nitrogen source. The addition of ED changed the morphology of carbon from spherical to a net-cross structure. A CV study demonstrates that nitrogen-doped carbons significantly improve the catalytic activity of the V(IV)/V(V) redox reaction compared with undoped pristine carbons. The enhanced activity is attributed to the formation of the active nitrogen functional group pyridinic-N, as confirmed by XPS analysis.

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